A Mystery of Criticality in Ternary Aqueous Solutions of 3-Methylpyridine and Sodium Bromide: A Multicritical Point or Non-Equilibrium Micro-Phase Separation?

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Some time ago, crossover from Ising critical behavior to mean-field behavior in the susceptibility of ternary solutions of water, 3-methylpyridine, and sodium bromide [Phys. Rev. Lett. 85, 2336-2339 (2000)] was deduced from light-scattering measurements. The crossover was found to be more pronounced with increase of the salt concentration. This result was interpreted as the emergence of a mean-field multicritical point on the critical line at a salt concentration of about 17 mass %. The mean-field behavior of the susceptibility was accompanied by a strong "background" light scattering, which was attributed to a micro-heterogeneous structure in the one-phase region. Moreover, a soup-like substance was observed on the liquid-liquid interface [Chem. Phys. -- Phys. Chem., 3, 829 (2001)]. The amount of the interfacial substance reached maximum at the range of concentrations close to the assumed multicritical point. However, some recent studies performed by other investigators [Gutkowski, Bianchi, and Japas, to be published] did not find a point with mean-field behavior on the critical line, although a minimum cutoff wave number was observed at 16.5 mass % of sodium bromide [Wagner, Stanga, and Schröer, Chem. Phys. --Phys. Chem., 4, 5300 (2002)]. To resolve this apparent contradiction, we have conducted additional, more accurate and more comprehensive studies of static and dynamic light scattering in this system. We have found that the ultrasonic agitation (that was also used to homogenize the sample in our previous study) may lead to the appearance of a non-equilibrium mesoscopic length in the solution and to the additional background scattering. Effects of impurities and the equilibration time have been also studied. A similarity with yet unresolved mysteries in behavior of some other near-critical ionic solutions as well as in non-critical tert-butanol aqueous solutions will be discussed.

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